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HIGH TEMPERATURE REACTION KINETICS OF BORON OXIDES

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13. ABSTRACT (Maximum 200 words)

Experiments using laser photolysis of water vapor to probe H+OH recombination chemistry in a mixture of combustion products of hydrogen, oxygen and phosphine are reported. When combustion products of phosphine are present, a large increase in the apparent H+OH recombination rate is observed. Progress was made in determining a baseline reaction model which describes the observed reaction rate. The thermochemical properties of 17 simple phosphorus species (possible combustion products of phosphine and oxygen) were assembled and the equilibrium densities of the phosphorus species were calculated under typical test conditions. The thermochemical properties of many of the phosphorus species have not been previously determined and were estimated from the results of ab initio quantum chemical calculations available in the literature. The six phosphorus species with the largest densities were used in the construction of a reaction model. Rate constant values were estimated using standard methods for the metathesis reactions and using simplified RRKM calculations to estimate the rates of recombination reactions. The increase in the observed rate of OH recovery was well described by this reaction set at the experimental conditions of 1970 K and 532 Torr. Two phosphorus containing recombination reactions appear to be rate limiting for H+OH recombination.

14. SUBJECT TERMS

Reaction rates, phosphine, phosporus oxide, recombination, kinetics, photolysis, thermochemical, rate constant.

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SUMMARY OF RESEARCH PROGRESS

OBJECTIVE

Catalysis of heat-releasing H+OH recombination in the nozzle section of a SCRAM-jet could potentially increase the fuel efficiency and therefore the thrust of a hydrogen-fuelled, air-breathing, hypersonic aircraft. The oxides of non-metal elements are potential catalysts for the recombination of H and OH. In particular, phosphine combustion products are found to substantially increase the rate of disappearance of excess OH when present in a mixture of partially photolyzed water vapor. The objective of this research program is to determine equilibrium densities of phosphorus combustion products present in the gas phase when phosphine is burned with oxygen, construct a reaction model including the most abundant phosphorus species, determine the rate constants for reactions of phosphorus combustion products in a high temperature gas and identify the mechanism by which phosphorus combustion products increase the disappearance rate of excess OH density in a water photolysis experiment.

RESULTS

Hydrogen reacts with oxygen at high temperature to produce water vapor and a considerable amount of heat. In our combustion reactor, gas temperatures of 1400-2300 K are achieved at pressures of 300-700 Torr. At these temperatures the equilibrated combustion products consist of small but significant amounts of radicals such as OH and H. To probe the reaction chemistry of the combustion products, the equilibrated system is perturbed by laser photolysis of H_2O which substantially increases the pool of OH and H radicals. The return of the system to equilibrium is experimentally investigated by recording, as a function of time, the OH absorption of a frequency-doubled cw-dye laser probe beam producing 312 nm radiation. The OH absorption signal is recorded on a digital oscilloscope and transferred as a binary file to a computer for subsequent analysis.

Figure 1 shows the dramatic effect on the rate of recovery of the OH signal when PH_3 is added to the hydrogen fuel and burned with oxygen. Photolysis occurs at 0.1 ms on the graph and results in a very fast increase in OH density (the value plotted in Figure 1 is the change in OH density from the equilibrium level). When phosphine is not present in the hydrogen fuel stream, the OH signal is observed to relax back towards its equilibrium value at a slow rate and is represented by the black squares plotted in Figure 1. The rate at which OH returns to its equilibrium value is increased significantly by the addition of only 0.03% by volume phosphine in the hydrogen flow stream. Addition of larger flows of phosphine cause an even more dramatic increase in OH disappearance as demonstrated by the parametric series shown in Figure 1.

Reaction Model

The large change in the OH relaxation rate observed when phosphine is added to the hydrogen fuel suggests that phosphorus combustion products are participating in the H+OH recombination process probably by opening alternate channels for recombination to occur. To further analyze the experimental OH decay data a kinetic model was constructed. As a first step in constructing the model, a list of phosphorus species which could potentially participate in the reaction chemistry was assembled. Table 1 lists these species along with their heats of formation at 0 K and entropies at 298.15 K. The thermodynamic quantities of a few of the listed species are reported in JANAF Tables and these values are included in Table 1. Phosphorus species which do not have a JANAF Table entry were estimated from quantum chemical calculations reported in the literature.

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Table 1. Estimated heats of formation at 0 K (Del Hf) and entropies at 298.15 K (S298) for phosphorus compounds in kJ/mol.

Species	Del Hf	S298	Species	Del Hf	S298
$HOPO_2$	-784	0.255	HPO	-75	0.216
P_2O_3	-655	0.311	PO	-23	0.212
HOPO	-524	0.241	PH_3	31	0.210
PO_3	-487	0.245	P_4	66	0.280
PO_2	-311	0.254	P_2O	90	0.236
H_2POH	-217	0.229	PH_2	129	0.213
HPOH	-117	0.230	P_2	145	0.218
P_2O_2	-96	0.291	PH	255	0.196
			P	316	0.163

The heats of formation and the entropies for each phosphorus compound were used to calculate a set of coefficients for thermochemical polynomials. From the thermochemical polynomials the free energy of formation for each phosphorus compound was calculated given the experimentally achieved gas temperature of 1970 K. Finally, the equilibrium densities of the selected phosphorus species were calculated given typical experimental conditions of 1970 K, 532 Torr and a phosphine fuel fraction of 0.001. Table 2 gives the equilibrium densities of phosphorus containing species thus calculated, along with the major species of hydrogen/oxygen combustion for the experimental conditions given above. From Table 2 it is clear that the equilibrium densities of many of the selected phosphorus species are too small to participate in reactions which could possibly cause the observed OH decay shown in Figure 1. In fact, the equilibrium density calculations show that the three species, PO_2, HOPO and $HOPO_2$, comprise over 99% of the phosphorus containing species present in the gas phase under the conditions of our experimental studies. Therefore, a smaller species list was chosen consisting of PO, PO_2, HOPO, $HOPO_2$, PO_3 and P_2O_3 from which a reaction set was assembled.

Table 2. Calculated equilibrium densities (mol/cm^3) of combustion products.

$[H_2O]-$	2E-06	$[PO_2]-$	3E-10	$[PH]-$	7E-18
$[H_2]-$	6E-08	$[HOPO]-$	7E-10	$[PH_2]-$	2E-18
$[O_2]-$	4E-10	$[HOPO_2]-$	1E-09	$[P_2]-$	5E-20
$[OH]-$	3E-09	$[PO]-$	1E-12	$[HPOH]-$	2E-18
$[H]-$	7E-10	$[PO_3]-$	1E-13	$[PH_3]-$	1E-20
$[O]-$	3E-11	$[HPO]-$	1E-15	$[H_2POH]-$	2E-20
$[HO_2]-$	7E-14	$[P_2O_3]-$	5E-16	$[P_2O_2]-$	1E-24
		$[P]-$	4E-16	$[P_2O]-$	2E-25
				$[P_4]-$	8E-36

A reaction set was systematically assembled by writing a computer program to list all the bimolecular reactions (including recombination reactions) possible among the species set consisting of H_2O, H_2, O_2, H, OH, O, HO_2, PO, PO_2, HOPO, $HOPO_2$, PO_3 and P_2O_3. From this reaction set, those reactions which have a positive heat of reaction were excluded along with those reactions which did not have a phosphorus species participating as a reactant. Furthermore, those reactions which involved the breaking of more than one chemical bond were also eliminated. The final list of 40 phosphorus reactions is given in Table 3 along with 13 reactions which describe hydrogen / oxygen combustion.

Finally, the rate constants for the bimolecular metathesis reactions listed in Table 3 were estimated using standard procedures.[1] The ternary recombination reactions were estimated using a simplified version of RRKM theory. The values of the reverse rate constants were calculated as needed from the equilibrium constants and the forward rate constants.

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[1] S.W. Benson, "Thermochemical Kinetics", (Wiley, NY), 1976.

Table 3. Reaction set used to analyzed OH decay data.

Rxn #	Reaction	Rxn #	Reaction
1	H + H = H2	27	H2 + PO3 = H + HOPO2
2	O + O = O2	28	O2 + PO = O + PO2
3	H + O = OH	29	O2 + HOPO = O + HOPO2
4	H + OH = H2O	30	H + HOPO = H2 + PO2
5	H + O2 = HO2	31	H + PO3 = O + HOPO
6	H + O2 = OH + O	32	H + PO3 = OH + PO2
7	OH + H2 = H2O + H	33	H + P2O3 = PO + HOPO
8	OH + OH = O + H2O	34	O + PO3 = O2 + PO2
9	O + H2 = OH + H	35	O + P2O3 = PO + PO3
10	HO2 + H = OH + OH	36	O + P2O3 = PO2 + PO2
11	HO2 + H = H2 + O2	37	OH + PO = H + PO2
12	HO2 + O = O2 + OH	38	OH + PO2 = O + HOPO
13	HO2 + OH = H2O + O2	39	OH + HOPO = H2O + PO2
14	O2 + PO = PO3	40	OH + HOPO = H + HOPO2
15	H + PO2 = HOPO	41	OH + PO3 = O + HOPO2
16	H + PO3 = HOPO2	42	OH + P2O3 = PO + HOPO2
17	O + PO = PO2	43	OH + P2O3 = PO2 + HOPO
18	O + PO2 = PO3	44	HO2 + PO = O + HOPO
19	O + HOPO = HOPO2	45	HO2 + PO = OH + PO2
20	OH + PO = HOPO	46	HO2 + PO2 = O2 + HOPO
21	OH + PO2 = HOPO2	47	HO2 + PO2 = O + HOPO2
22	HO2 + PO = HOPO2	48	HO2 + PO2 = OH + PO3
23	PO + PO2 = P2O3	49	HO2 + HOPO = OH + HOPO2
24	H2O + PO = H + HOPO	50	HO2 + PO3 = O2 + HOPO2
25	H2O + PO2 = H + HOPO2	51	PO + HOPO2 = PO2 + HOPO
26	H2O + PO3 = OH + HOPO2	52	PO + PO3 = PO2 + PO2
		53	HOPO + PO3 = PO2 + HOPO2

Sensitivity Analysis

A sensitivity analysis of the OH decay profile was performed using the reaction set listed in Table 3 and the experimentally realized conditions of 532 Torr, 1970 K and a phosphine fuel fraction of 0.001. Here, sensitivity is defined as the fractional change in the OH signal divided by the fractional change in the value of a particular reaction rate constant. The result of this analysis shows that two reactions,

$$H + PO2 \rightarrow HOPO \qquad \text{(Rxn 15)}$$

and $HO + PO_2 \rightarrow HOPO_2$, (Rxn 21)

determine the shape of the OH signal to a much greater extent than the other reactions.

Data Analysis

The rate constants for reactions 15 and 21 were used as parameters in a data fitting routine. In a series of experiments the phosphine flow rate was increased from 0 to 0.15 per cent of the hydrogen fuel flow rate. For each phosphine flow rate an H_2O photolysis experiment

was performed and the OH decay was recorded. In this analysis the initial amount of OH and H formed by photolysis, DelOH, was treated as a fitting parameter along with the two rate constants, k_{15} and k_{21}.

Figure 2 shows the OH decay data along with the model calculation for one of the phosphine data sets. The mean of three measurements gave a rate constant value of 3.1×10^{16} $cm^6 mol^{-2} s^{-1}$ for k_{15} and 1.5×10^{16} $cm^6 mol^{-2} s^{-1}$ for k_{21} at 1970 K. These rate constant values are a factor of 2.5 and 4.7, respectively, larger than the values estimated using RRKM theory. In this series of experiments our purpose was not to determine accurate rate constant values but rather to test the results of the rate constant estimation process. It is reassuring that the data fit values of the rate constants k_{15} and k_{21} are within a factor of 10 of values estimated by simplified RRKM calculations. A more accurate determination of rate constant values will be done in the future.

The sensitivity analysis has identified reactions 15 and 21 as far more important in determining the shape of the OH decay signal than other reactions. However, these two reactions do not proceed in isolation, for by themselves they can not restore the reaction system to chemical equilibrium. Therefore, a calculation was performed to determine the net rate of each of the 53 reactions 5×10^{-4} seconds after H_2O photolysis. The calculation assumed typical experimental conditions of 1970 K, 532 Torr and a phosphine fuel fraction of 0.001. A calculation assuming no phosphine addition to the hydrogen fuel was performed for comparison purposes. When phosphine combustion products are present the net rate of reactions 15, 21 and 30 are predominantly active in the forward direction, the rate of reaction 7 is markedly increased in the forward direction and the rate of reaction 25 proceeds prominently in the reverse direction.

Two reaction sequences can be written which use only reactions from the set of five most active. Both sequences provide an alternative reaction mechanism for the net recombination of H and OH to form water vapor. The rate of the first sequence

$OH + PO_2 \rightarrow HOPO_2$ (Rxn 21)

$H + HOPO_2 \rightarrow H_2O + PO_2$ (-Rxn 25)

will be limited by the rate of the ternary reaction step (Rxn 21) which consumes PO_2. The two-body reaction (-Rxn 25) completes the H+OH recombination process by converting the product of Rxn 21, $HOPO_2$, back to PO_2. The second reaction sequence

$$H + PO_2 \rightarrow HOPO \qquad \text{(Rxn 15)}$$

$$OH + H_2 \rightarrow H_2O + H \qquad \text{(Rxn 7)}$$

$$H + HOPO \rightarrow H_2 + PO_2 \qquad \text{(Rxn 30)}$$

consists of three steps, one of them (Rxn 7) does not include a phosphorus containing species as reactant or product. Once again the ternary step (Rxn 15) will limit the overall rate of the sequence while the other two reactions return the product (HOPO) of this reaction back to the starting reagent (PO_2 again). A third sequence may be considered in which reactions 7 and 30 are replaced by

$$HOPO + OH \rightarrow PO_2 + H_2O. \qquad \text{(Rxn 39)}$$
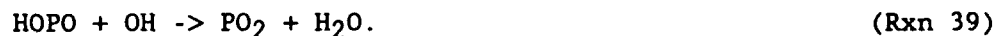
However, reaction 39 does not appear to be as rapid as the combination of reactions 7 and 30 under the experimental conditions of this study.

PERSONNEL

A.J Twarowski - Principal Investigator

PUBLICATIONS

1. A.J. Twarowski, "The Influence of Phosphorus Oxides and Acids on the Rate of H+OH Recombination", J. Phys. Chem., manuscript in preparation.